THERMOPLASTICALLY PROCESSABLE POLYAMIDES
[Thermoplastisch verabeitbare Polyamide]

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THERMOPLASTICALLY PROCESSABLE POLYAMIDES

[Thermoplastisch verarbeitbare Polyamide]

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It is known to targetedly produce polymer systems, in particular polyolefin systems, with branched-chain structures.   /2*

Through the choice of the monomers used and the polymerization technique, an infinite variety of chain structures can be obtained. The type of chain branching influences the rheology of the polymer melt and the properties of the finished products produced from said melts, for example, the melting and solubility behavior, as well as the mechanical properties, for example, the stiffness, toughness, and stress-strain behavior.

GB 750 629 describes the production of polyamide from dicarboxylic acids and diamines as their main components, in particular the production of PA-66, which contain trimesic acid in an amount of 0.3 to 3.8 mol%, with an equivalent amount of diamine condensed in.

The UK Patent GB 749 479 describes the production of polyamides from diamine and dicarboxylic acids as their main components, in particular the production of PA-66, which contain bishexamethylene triamine in combination with a dicarboxylic acid, preferably in an equivalent amount. The objective of these two prior-art procedures is to increase the melt viscosity of the polyamides.

It was discovered, however, that these procedures are unsuitable for practical application since they invariably entail the simultaneous formation of crosslinked fractions which are deposited along the wall of the reactor vessel and which, during the processing of the melt, for example, to produce sheeting materials, lead to a considerably increased formation of inhomogeneities ("fish eyes").

The U.S. Patent US 1,263,952 describes polyamide masses with defined percentages by weight of mono- and trifunctional compounds. In the examples, the only monomer mentioned is 6.6 salt.

This basically also applies to BE 641 630, according to which the monofunctional building blocks additionally contain secondary amino groups in order to improve the receptivity to acid dyes.

So far, not much is known about targetedly branched thermoplastically processable polyamides. In connection with the discussion of A-B polyamides (PA-6, PA-11 and PA-12), the "Kunststoffhandbuch" ["Plastics Manual"], Vol. VI, Polyamides (C. Hanser Verlag Munich 1966, page 15), states that a polyfunctional compound which contains only one type

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* [Numbers in the margin indicate pagination of the original text.]

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of terminal groups, for example, group B, can necessarily only lead to a branched macromolecule. Model considerations on this subject indicate that such macromolecules have a defined branch point.

DE-OS 2 732 329 describes polycaprolactam and copolymers which also contain salts of diamines and dicarboxylic acids, for example, of hexamethylenediamine and terephthalic acid (Example 2), and triamines with the structure $H_2N-R-NH-R-NH_2$ in the monomer mixture. The examples show that equimolar amounts of triamine and additional carboxylic acid are used (Examples 1b and 2C). In practice, however, it was found that formulations, which also contain a monomer mixture of salts of diamines and dicarboxylic acids (Example 1b), have the tendency to form crosslinked structures, which manifests itself in the formation of gel particles and deposits on the wall of the reactor vessel. Although the simultaneous use of monomer chain-length regulators does reduce the formation of crosslinked polymer fractions, such fractions still form in quantities that have a negative effect. This is particularly evident if several polymerization batches are to be polymerized one after the other in the same condensing vessel, i.e., in the series production of industrial batches. The crosslinked polymer fractions that form are initially deposited along the wall of the condensing vessel, and, from one batch to the next, the discharged polymer becomes more and more inhomogeneous (has more and more fish eyes). Processability and quality decrease accordingly.

DE-OS 24 06 491 relates to bicomponent fibers consisting mainly of polycaprolactam. To achieve the crimp properties desired, pure PA-6 is spun with PA-6 copolyamide which, as a co-component, contains approximately 10 to 20 wt% of the salt of dimerized fatty acid and diaminohexane. The mentioned low molar fraction of trimerized fatty acid is an invariably forming impurity in the production of dimerized fatty acid and does not affect the crimp properties. It can, however, impair the polymer quality due to the formation of gel particles.

In DE-OS 37 14 607, lactam polyamides are described, for the production of which preferably 0.2 to 2 wt%, preferably 0.3 to 1.0 wt%, of α-amino-ε-caprolactam in combination with an approximately equivalent amount of dicarboxylic acid as a polymerization accelerator are used. This special polyamide building block contains the functionalities -COOH and -NH₂ in the equivalent ratio of 1:2. The -COOH groups lacking for a complete condensation of all terminal groups are deliberately added. Thus, it is possible for crosslinked polymer fractions to form at the same time. As a result, the fraction of this polymer addition must be limited to the very low value of less than 2 wt%, preferably to 0.3 to 1 wt%.

Overall, this indicates that in cases in which

A. an at least trifunctional compound is added to polyamides from salts (diamine + dicarboxylic acid) or to polyamides which also contain monomers of the corresponding salt pairs or

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B. an at least trifunctional compound (amine or carboxylic acid) is added, which also contains the at least

bifunctionally active compound that is sufficiently active to condense with said trifunctional compound in a nearly equivalent

ratio, and in particular

C. the measures discussed under A and B are combined,

it will not be possible to reproducibly manufacture thermoplastically processable polyamide from high quality, i.e., in several

batches one after the other.

Thus, the problem to be solved by the present invention was to produce high-molecular, branched-chain polyamide from

high quality that can be reproducibly manufactured in a large number of consecutive batches and that have at least 50 wt% of

polymer chains with more than one branching.

Surprisingly, it was found that the thermoplastic polyamides as in Claim 1 no longer have the disadvantages of the prior

art described above.

Thus the invention relates to thermoplastically processable polyamides from amino acids and/or lactams as basic units;

said thermoplastically processable polyamides being obtainable by means of hydrolytic polymerization wherein at least

50 wt% of the polymer molecules have more than one chain branching, which polyamides can be obtained by adding

branching-causing components in the following composition to the melt of the base monomers:

a) 5 to 150 µmol/g polymer of an at least trifunctional monomer that consists of an amine or a carboxylic acid and

b) 2 to 100 µmol/g polymer of an at least bifunctional monomer that consists of a carboxylic acid or an amine, under

the condition that, if a) is an amine, b) must be a carboxylic acid, and if a) is a carboxylic acid, b) must be an amine, and

optionally

c) 5 to 450 µmol/g polymer of a monomer which, during a conventional polycondensation, acts monofunctionally.

It is an essential feature of this invention that exclusively amino acids and lactams may be used as base monomers.

Another feature essential to this invention is that the additional chain building blocks participate to an important extent in

determining the structure of the polymer chains, i.e., their degree of branching, their mean molecular weight, and the type of

their chain ends, and therefore must be used in a defined molar ratio relative to one another that is essential to this invention.

The polyamides according to the present invention are preferably obtained in such a manner that a molar ratio of

component a) to component b) of at least 1 is maintained if component a) is trifunctional and component b) is bifunctional,

and that a molar ratio of at least 2 is maintained if component a) and component b) are trifunctional.

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According to another preferred embodiment, the polyamides according to the present invention are obtained in such a manner that component a) contains bifunctional compounds in such a molar fraction that no more than 50 wt% of linear polymer chains are formed.

According to yet another preferred embodiment according to the present invention, the polyamides are obtained in such a manner that monofunctional compounds c) with a functionality according to components a) in a molar fraction that does not exceed a) are simultaneously used.

Preferably, the polyamides according to the present invention are also obtained in such a manner that monofunctional compounds c) with the terminal groups according to b) in a molar fraction that is calculated according to the following formula are used
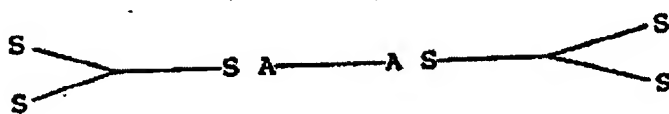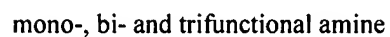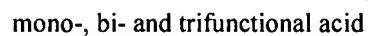
$$c) = m_{a)}f_{a)} - m_{b)}f_{b)} + 100$$

wherein $m_{a)}$ and $m_{b)}$ stand for the molar fractions of compounds a) and b) (expressed in µmol/g polymer) and $f_{a)}$ and $f_{b)}$ stand for the functionalities of the compounds.

According to another preferred embodiment of the present invention, the polyamides are obtained in such a manner that monomer compounds according to a) and b) are used and that the conditions according to Claims 4 and 5 are maintained for the monofunctional compounds c) concerned.

A precise analysis of the problem posed has shown why the branched polyamides known from the prior art always have a tendency toward gel formation and crosslinkage and why this phenomenon does not occur with the polyamides according to the present invention. The reason is that if a polyfunctional, for example, a trifunctional, compound with only one type of terminal groups (for example, -COOH) is added to a melt of pure amino acid (and/or lactam), a polymer molecule grows in 3 defined directions, which polymer molecule always carries the -COOH group on its chain end. Since -COOH groups under normal condensation conditions do not react with one another, no crosslinkage can occur. It is now possible to specifically   /4 determine how the chain structure that forms changes if diamine in different molar fractions relative to the tricarboxylic acid is added to the melt.

The following example structures clearly differentiate the polyamides according to the present invention from those of the prior art. The number of the components shown corresponds directly to their molar ratio. The actual chain members are obviously derived from the amino acids which are interposed between these special units but which never change the terminal group ratios. The symbols below have the following meaning:

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——S S——— S S—⊤— S   mono-, bi- and trifunctional acid
                  |
                  S

———A A——— A A—⊤—A   mono-, bi- and trifunctional amine
                  |
                  A

1. S⟍
      ⟍—S A———A S——⟨   (X)
    S⟋   S

In the statistical mean, chains with two branchings form; crosslinkage does not occur.

2. S⟍
      ⟩——S   A———A   S——⟨   S———S ‖
    S⟋   S
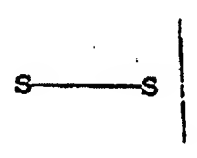
An examination of the potential combinations of these components shows that if this regulator system is chosen, chains with two and one branching(s) as well as purely linear chains form.

3.
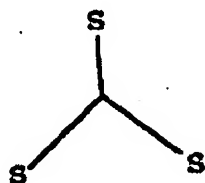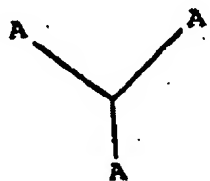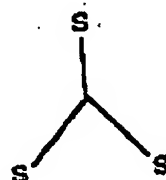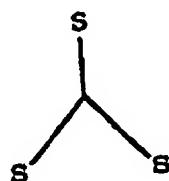
If this regulator system is chosen, highly branched polymer molecules with a broad molecular weight distribution with a   /5
mean degree of branching of 4 form.

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If a fraction of linear chains is additionally desired, for example, in order to increase the flowability of the melt, mono- and/or dicarboxylic acids in a defined molar fraction can be simultaneously used. In that case, polymer molecules of the linear, singly branched and doubly and triply branched type in a defined fraction are additionally obtained.

The schematic diagrams 1 and 3 also clearly show why the formation of crosslinked fractions is invariably observed in the state of the art, where salts are (also) used as monomers and where the functional groups, for example, are neutralized due to the formation of salt (for example, trimesic acid with diaminohexane).

The excess of amine or the presence of the stoichiometric fraction thereof, for example, relative to the carboxylic groups of trimesic acid is able to form a three-dimensionally crosslinked structure, as can be seen in the schematic diagrams 1 and 3 that are derived from Examples 1 and 3.

a) Schematic diagram 1, but in the salt pair as a monomer system.
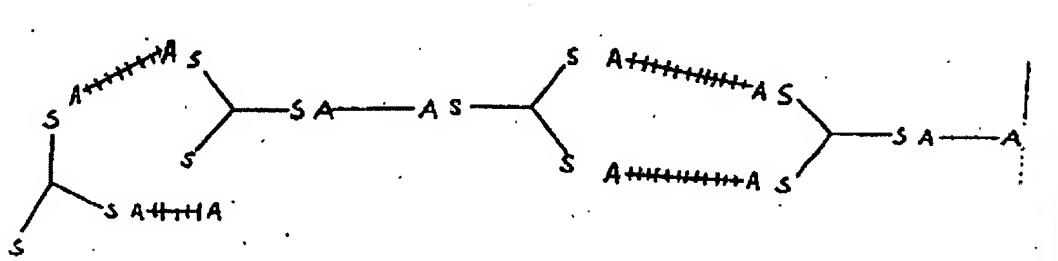
b) Schematic diagram 3 where trimesic acid is used in combination with triamine in a defined molar ratio but where the COOH groups of the trimesic acid are at the same time completely neutralized with diamine.
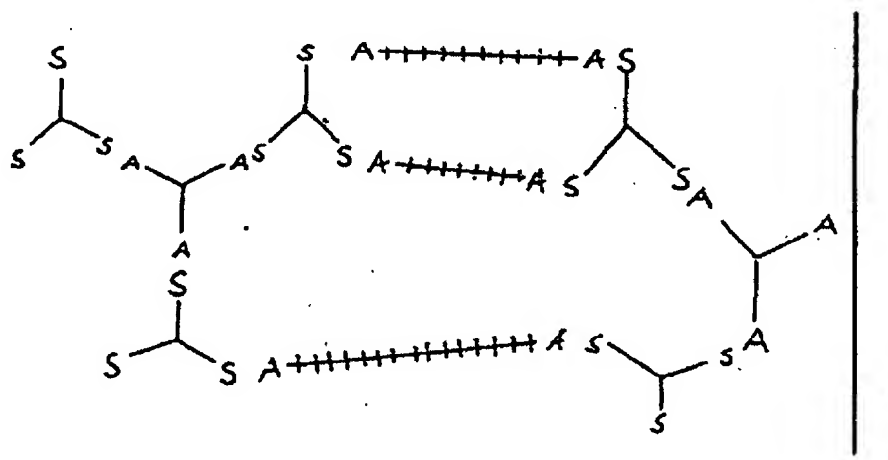
A ├┤┤┤┤┤ A are amine-terminated polyamide chains which can condense with the acid chain ends to form a 3-dimensional network.

If the branched polyamide mass according to the present invention is to have a certain concentration of functional terminal groups, for example, to specifically adjust the receptivity to acid dyes, monofunctional compounds, such as benzoic acid or cyclohexylamine, can also be incorporated into the polymerization formulation. Through the simultaneous use of these monofunctional compounds, a reduction of the degree of branching or the simultaneous formation of linear chains in a defined fraction can also be achieved. In this context, it is important to note that it matters whether the monofunctional compound contains the terminal groups in accordance with components a) or b). The effect of monofunctional compounds will be explained in schematic diagram 4, using example structure 1 as a basis:
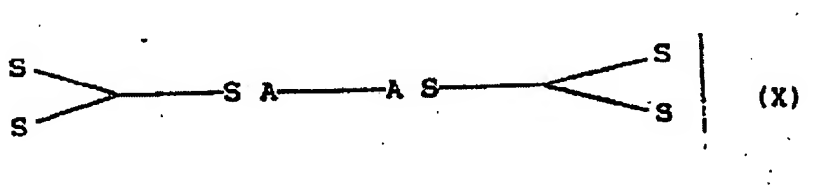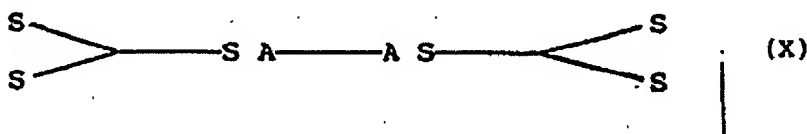
4a) The monofunctional compound is a monocarboxylic acid, —— s. Even small fraction influence the structural formation of the polyamide chain molecules in that, in addition to (X), for example, simultaneously the following structures form:
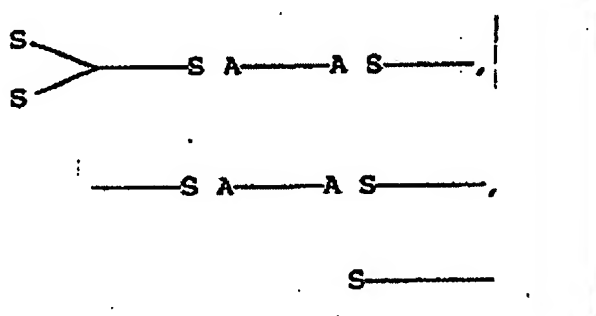

4b) The monofunctional compound is an amine with a condensable -NH₂ group, for example, —— A.

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Since this polymer molecule (X) is acid-terminated, A can initially react with S, without considerably interfering with the structural formation. Initially, only the functional terminal groups are influenced to the extent desired. If, on the other hand, more than 4 —— A per (X) are used, structures of the following type form:
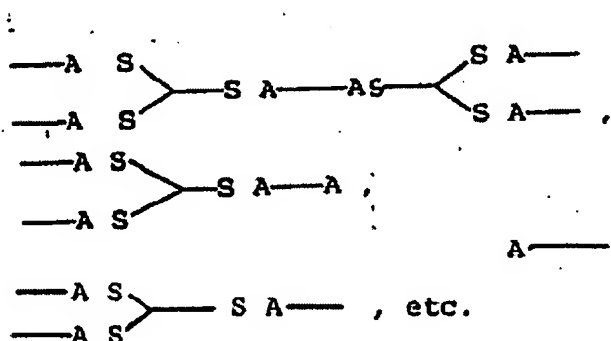
If, for example, a high receptivity to acid dyes is desired in this system, compounds with a condensable and a sterically shielded amino group, such as
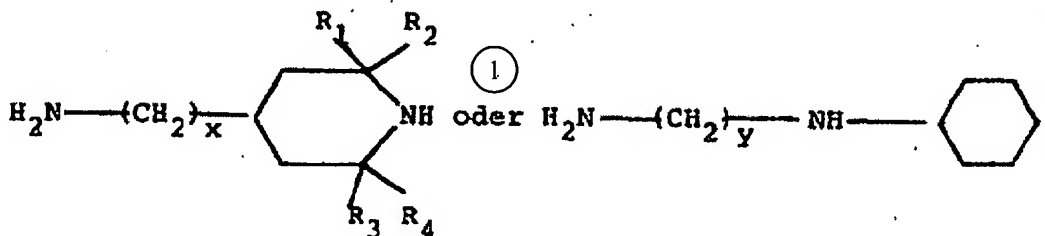
Key: | Or

should be chosen, where x is 0 to 12 and y is 2 to 12 and where R_1, R_2, R_3 and R_4 stand for identical or different alkyl groups with 1 to 4 carbon atoms, in particular methyl groups. In the context of this invention, these are considered to be monofunctional.

As to the formation of the branched polymer molecules according to the present invention, obviously the normal laws of chain growth, such as are known for the condensation polymers, apply. Specifically, the following should be noted:

1. If the branching component contains COOH groups that are in the type of neighboring positions relative to one another so as to preferably lead to the formation of imide bonds, for example, ortho positions on the benzene ring, the number of the polymer arms is reduced to the same extent that imide structures are formed.

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2. If, as in the schematic diagram 4b, a considerable fraction of monofunctional compounds is simultaneously used, the terminal phase of the polycondensation reaction is markedly delayed. Many chain ends do not actively participate in the condensation.

3. Compared to the linear chain molecules, the highly branched chain molecules have a markedly higher molecular weight since many preformed structural elements recombine in the terminal phase of the structural formation.

4. However, since the recombination of preformed structural elements is never complete, invariably a small quantity of pure polyaminocarboxylic acid and thus a few short linear chains remain.

The surprising discovery that, in the complete absence of salts ω of diamine and dicarboxylic acid as base monomers, but with the exclusive use of amino acid and/or lactam, it is possible to reproducibly produce branched-chain, thermoplastically processable polyamides with a considerable spectrum of variations in their properties if a combined regulator system according to the present invention is employed, led to novel polyamides with a highly diverse spectrum of properties. Thus, it is possible, for example, to increase the flowability through the novel chain structure. If copolyamides are produced, for example, from 6-lactam and ω-aminoundecanoic acid or ω-aminododecanoic acid with the use of the chain structure regulation according to the present invention, the melting point of said copolyamides can be predetermined by way of the mixing ratio of the base monomers, and the type and concentration of the terminal groups can be predetermined by the targeted choice of the regulator system. Thus, through the possible high concentration of functional terminal groups and their type, it is possible to adapt the adhesion to the greatest number of different substrates to the practical requirements. An increased concentration of -COOH also allows an improved adhesion to glass fibers and minerals that carry an aminosilane layer.

In the production of polymer blends, it is also often useful to have available a defined high concentration of functional groups which can mediate the compatibility of the polymer phases, for example, by means of ion binding, the formation of addition compound or chemical reaction, for example, of -NH$_2$ with NCO-. Through a suitable choice of component c), it is also possible to specifically vary the receptivity to acid dyes within a wide range. If the regulator system is chosen to ensure that short linear polymer molecules in a defined molar fraction form at the same time, it is possible to polymerize, for example, in the batch process over a large number of batch sequences, without the risk of any deposits forming along the wall of the polycondensation vessel or partially crosslinked products with fish-eye defects being produced, as used to be the case in the prior art.

The production of the polyamides according to the present invention takes place according the generally known production methods, preferably in the batch process. Since first the components according to a), b) and optionally c) are incorporated into the growing polymer chains and since, during the degassing phase, these preformed segments gradually combine to form the final structure, the time of the degassing phase can be markedly longer. However, through application of a vacuum and continuous renewal of the surface as well as by ensuring a favorable temperature profile, the length of the degassing phase can in turn be shortened again. If, on the other hand, lactams are used as monomers, which is actually most commonly the case, the ring-opening reaction is distinctly accelerated as a result of the presence of the branching-causing components with their functional terminal groups. The choice of the branching-causing components and the monofunctional components must, of course, also take into consideration the monomers to be used.

If the monomer requires a very high melting temperature to ensure opening of the ring (example: 12-lactam), preferably components a), b) and c) with a low volatility are to be used.
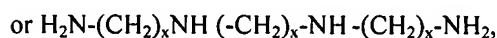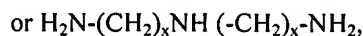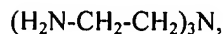
The base monomers to be used include all lactams and amino acids suitable for the production of polyamides, for example, caprolactam, enantholactam, laurolactam, dodecalactam as well as the relevant amino acid and aminoundecanoic acid and p-(aminomethyl)benzoic acid.

Component a) of the present invention must have at least 3 functional groups of the same type (-NH$_2$ or -COOH). It should be readily soluble in the melt of the monomers or it should be brought into solution by means of salt formation with component b) and/or c). It should be noted that in the usual polycondensation reaction with dicarboxylic acids with -COOH groups in ortho position, for example, on the benzene ring, imide formation results, which reduces the number of the chair branchings that can form. Suitable components a) include: trimesic acid, trimerized fatty acids (produced from oleic acid) with 50 to 60, especially 54, C atoms, naphthalene polycarboxylic acids, for example, naphthalene-1,3,5,7-tetracarboxylic acid, the acid or its esters of the structure
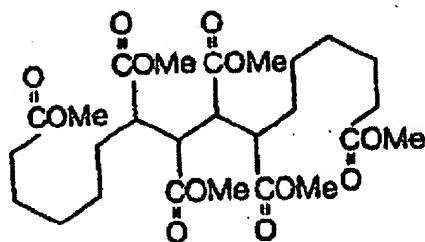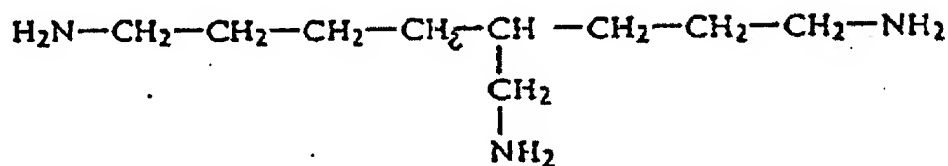
where Me stands for the $-CH_3$ group. Quite generally, it is, of course, possible to use the usual esters of the polycarboxylic acids with short-chain alcohols.

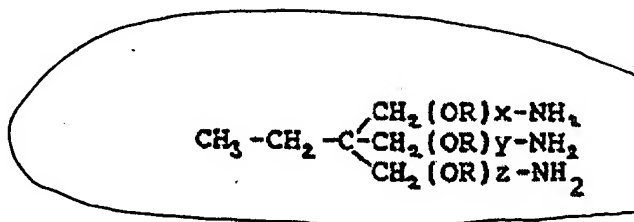Amines with 3 condensable groups $-NH_2$ or $-NH-$ are, for example,

$(H_2N-CH_2-CH_2)_3N$,

or $H_2N-(CH_2)_xNH\ (-CH_2)_x-NH_2$,

or $H_2N-(CH_2)_xNH\ (-CH_2)_x-NH\ -(CH_2)_x-NH_2$,

or $H_2N-(CH_2)_xNH\ (-CH_2)_x-NH\ -(CH_2)_x-NH\ -(CH_2)_x-NH_2$,

where x stands for 2 to 13.

$$H_2N-CH_2-CH_2-CH_2-CH_2-CH\ -CH_2-CH_2-CH_2-NH_2$$
$$|$$
$$CH_2$$
$$|$$
$$NH_2$$

or

$$CH_3-CH_2-C\begin{matrix} CH_2(OR)x-NH_2 \\ CH_2(OR)y-NH_2 \\ CH_2(OR)z-NH_2 \end{matrix}$$

where x, y and z each stand for 1 to 15 and R is an ethyl, butyl or isopropyl group.

As components according to b), the same compounds that have already been described under a) can be used. In addition, it is possible to use bifunctional compounds that contain exclusively one type of functional terminal groups. These are dicarboxylic acids, for example, adipic acid, azelaic acid, sebacic acid, dodecanoic diacid, terephthalic acid, isophthalic acid and dimerized fatty acids, and diamines, for example, hexanediamine, xylylenediamine, m- and p-aminodicylcohexyl methane and corresponding alkyl-substituted products. The monofunctional compounds to be used include the usual monoamines and monocarboxylic acids, for example, benzoic acid, pelargonic acid, lauric acid, 2-ethylhexanoic acid, cyclohexylamine, alkylamines, for example, tridecylamine, and benzylamine. Monofunctional amines within the meaning of the present invention as it relates to the hydrolytic condensability of the amino group also include amines which, in addition to a free amino group, have a sterically shielded amino group, for example, the amines
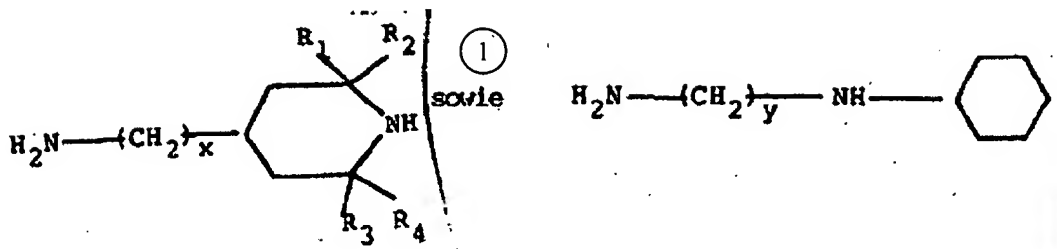
Key: 1   And

where x stands for 0 to 12, in particular for 0, and y stands for 2 to 12, in particular for 3, and where R_1 to R_4 stand for identical or different alkyl groups with 1 to 4 carbon atoms.

Especially preferred is the following amine:
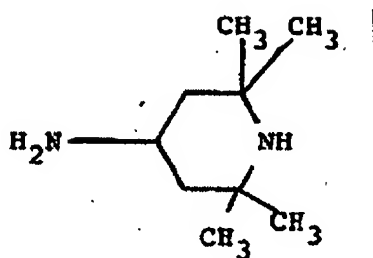
The following examples will explain the invention.

To implement these examples, the following basic units are used:

Aminolauric acid	ALS
Laurolactam	LL
Aminocaproic acid	ACS
Caprolactam	CL
Aminoundecanoic acid	AUS
The salt of hexamethylenediamine and azelaic acid	6.9 salt

To regulate the structural formation, the following components a), b) and c) are used:

Trimesic acid	TMS
Nitrilotriethaneamine [sic]	N-TEA
Azelaic acid	AZ
Adipic acid	ADS
Diaminohexane	HMD
Benzoic acid	BZ
3-Amino-1-cyclohexylaminopropane	L-252
Tridecylamine	Trida

Examples 1 to 8

These examples describe the production of polyamides on a laboratory scale.

The monomers and the additional components are weighed out into a condensing tube. The mixture is melted under nitrogen and polycondensed while stirring and gradually increasing the temperature.

These experiments demonstrate the influence of the different monomers and units on the polycondensation behavior as well as the structures that can be obtained.

The results of these experiments are summarized in Table 1, with Table 1a showing the polymerization formulas, Table 1b the polycondensation conditions, and Table 1c the results of the analyses.

The experiments designated with "V" are comparative experiments.

When experiments V1 and V2 were carried out according to the prior art, we used the 6,9 salt as the monomer and N-TEA which is readily soluble in the polymer melt as component a) alone as well as in combination with benzoic acid. The description of the course of the reaction reveals that crosslinkage sets in after only a short time.

Experiments V3 to V6 involve singly branched polyamides; because of the favorable polycondensation properties, a mixture of ACS and ALS in the molar ratio of 1:1 was used as the monomer.

When amino acids are used as monomers, no crosslinkage occurs when a trifunctional component is added.

Comparative Example 3 shows that due to the low solubility of the trimesic acid, the resultant polymer melt is not completely clear.

By combining trimesic acid (TMS) with a diamine with only one polycondensable amine function, it is possible for salt to form, and the resultant polymer melt is clear. The diamines to be used are benzylamine, cyclohexylamine or tridecylamine.

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The analytical results show that the concentration of these additional components influences the mean molecular weight as expected.

Examples No. 7 and No. 8 are examples according to the present invention. By combining the trifunctional component a), i.e., N-TEA, with AZ as component b), polymer chains with two branch points form. By simultaneously using monoamine as component c), linear polymer chains in the predetermined concentration result. As the analytical results demonstrate, readily flowable products are obtained in spite of the high molecular weight.

These experiments show that in the course of the polycondensation, the chosen reactive groups of the polyfunctional components a) and b) do not enter into secondary reactions, therefore not leading, for example, to the formation of imides. Thus, in the context of the present invention, for example, 1,2-, 1,2,4- and 1,2,4,5-benzenepolycarboxylic acids, nitrolotriacetic acid, ethylenediaminetetraacetic acid, and butane-1,2,3,4-tetracarboxylic acid are therefore unsuitable. Suitable according to the present invention, however, are--in addition to the already described units--all nonvolatile or only slightly volatile, thermally sufficiently stable polyfunctional carboxylic acids and aliphatic amines that contain at least one functional group which is sterically not shielded.

Examples 9 to 20

The following examples 9 to 20 are experiments that were carried out on an industrial scale:

To carry out these experiments, known steel autoclaves heated with heat transfer oil and designed for excess pressure were used, and the polycondensation was carried out using conventional means under a nitrogen/water vapor atmosphere.

The details of the experiments are summarized in Table 2. Table 2a describes the polymerization formulas, Tables 2b/c describe the polymerization conditions and the results of the analysis, and Table 2d shows the results of the mechanical tests. The comparison of the mechanical values also lists the comparative experiments 19 and 20. In comparative experiment 19, the material corresponds to a polyamide-12 for standard injection molding applications and in comparative experiment 20 to a polyamide-6 for standard injection molding applications. A comparison of the mechanical properties indicates especially an increase in the tensile stress and a reduction of the elongation at break. These changes in the basic mechanical properties are especially obvious in the case of PA-12. In the case of PA-6, they can also be clearly seen, especially when dry, but they are reduced as the material absorbs moisture.

In addition, Table 2d also lists the results of the comparative experiments 19 and 20. The mechanical tests in comparative experiment 19 are carried out with test specimens made of polyamide-12 for standard injection molding applications and those in comparative experiment 20 are carried out using polyamide-6 for standard injection molding applications.

To clearly illustrate the influence of multiple branching on the basic mechanical properties, Figures 1 to 4 show a few stress-strain curves of the products according to the present invention. Also shown are the stress-strain properties of the standard injection molding materials made of PA-6 and PA-12. All stress-strain curves meet the requirements of DIN 53455, measured at 23°C and an elongation rate of 50 mm per minute.

The stress-strain curves of the products according to the present invention clearly demonstrate the increased strength in the region of the yield point. The examples also show that, as the branching density increases, the path of the stress-strain curve changes in such a manner that the decrease in strength is reduced after the "yield point." At higher branching densities and degrees of polymerization, it is even possible to observe that the strength does no longer decrease (Example 16) so that a defined yield point no longer exists. The products according to the present invention will therefore be suitable for use especially in applications that require materials with a relatively high strength at low elongation, which in practical applications is often required.

Table 1

a) Formulas

Experiment		Basic units			μMol/g	Components Polymer		
Type	No.	6.9 salt	ALS/ACS =1:1	Amt of Polymer in g	TMS	BZ	L-252	N-TEA
Comparison	1	+		60				60
"	2	+		60		120		60
"	3		+	70	60		-	
"	4		+	70	60		180	
"	5		+	70	40		120	
"	6		+	70	10		30	
			AUS		AZ		Trida	
Type	7		"	80	20		20	60
"	8		"	80	30		10	60

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b) Course of the reaction

No.	t (h)	T (°C)	t	T	t	T	t	T	Comments
1	1	200	0.2	240					Crosslinked
2	1	200	0.5	240	1	270			"
3	1	200	6	260	-	-			
4	0.5	180	1	210	2	240	1	260	Clear melt
5	1	200	2	240					"
6	1	200	2	240					"
7	1	200	2	240	1	260			"
8	1	200	2	240	1	260			"

c) Analytical values

No.	Solution viscosity η rel. 0.5% m-cresol	Melt viscosity 200/122.6 N Pa · s	Terminal groups $\mu eq/g$ - COOH	-NH$_2$
1				
2				
3	1.446	62	170	5
4	1.406	29	56	231
5	1.468	56	60	175
6	1.726	270	46	73
7	1.831	105	8	224
8	2.198	640	5	189

Table 2 /13

a) Polymerization formulas

Experiment No.	Basic units	Batch, kg	a) TMS	b) N-TEA	b) ADS	b) HMD	c) L-252	Mean degree of branching of the branched polymer fraction
9	ALS	8	60			30	120	2
10	ALS	8	90	30			180	4
11	ALS	8	92	30			190	3.8
12	ALS	8	60	30	60		170	3.0
13	ALS	40	56	28	46		176	3.0
14	CL	40	70			30	150	1.75
15	CL	40	100	30			210	3.25
16	CL	40	100	30			210	3.25
17	CL	42	56	28	46		176	300
18	CL	45	40	20	32		124	3.00

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b) Polymerization conditions   c) Polymer analysis (terminal groups)

Experiment No.	Pressure phase			Degassing		Solution viscosity η rel. (0.5% m-cresol)	Melt viscosity			Terminal groups µeq/g	
	Temp. °C	Time, h	Pressure, atü	Temp., °C	Time, h		Temp., °C	Load, N	Pa·s	-NHR	-COOH
9	220	1	10	240	8	1.72	220	122.6	390	135	22
10	220	1	10	240	8	1.92	220	122.6	440	219	14
11	220	1	10	240	6	1.71	-	-	-	224	24
12	220	1	10	250	6	1.765	260	122.6	390	160	27
13	220	2	10	250	7	1.71	-	-	-	203	23
14	260	1	10	260	6	1.68	-	-	-	130	19
15	260	1	10	260	6	1.85	-	-	-	154	27
*16	260	2	10	265	7	1.88	-	-	-	180	26
17	240	3	5	260	6	1.52	-	-	-	220	30
18	240	3	5	260	8	1.56	-	-	-	172	26

*Structure regulator system added in the form of an aqueous salt solution

d) Mechanical properties

Experiment No.	NBI		TS N/mm²	YS %	BS N/mm²	EB
	Dry	Conditioned				
9	5	5	38	23	41	235
10	4	4	49	33	47	30
11	4	7	44	16	35	32
12	-	-	50	15	44	32
13	-	-	41	32	37	56
Comparison 19	6	10	33	20	50	290
14	-	-	-	-	65	22
	-	-	-	-	*37	*100
15	-	-	36	10	-	-
			*28	*30	*47	*260
16	-	-	58	22	-	-
			*32	*30	*32	*55
17	-	-	65	30	-	-
			*37	*30	*37	*90
18	4	08	-	-	46	52
	-	-	*31	*30	*47	*300
Comparison 20	5	15	56	39	43	100
	-	-	*29	*30	*57	*260

The abbreviations have the following meaning:

TS-Tensile stress

YS-Yield strain

BS-Breaking strength

EB-Elongation at break

According to DIN 53455

NBI-Notched bar impact strength DIN 53453 (in kJ/m²)

* Measured values after conditioning

Claims

1. Thermoplastically processable polyamides from amino acids and/or lactams as basic units, said thermoplastically

processable polyamides being obtainable by means of hydrolytic polymerization, wherein at least 50 wt% of the polymer

molecules have more than one chain branching, characterized in that they can be obtained by adding branching-causing components in the following composition to the melt of the base monomers:

   a) 5 to 150 μmol/g polymer of an at least trifunctional monomer that consists of an amine or a carboxylic acid and

   b) 2 to 100 μmol/g polymer of an at least bifunctional monomer that consists of a carboxylic acid or an amine, under the condition that, if a) is an amine, b) must be a carboxylic acid, and if a) is a carboxylic acid, b) must be an amine, and optionally

   c) 5 to 450 μmol/g polymer of a monomer which, during a conventional polycondensation, acts monofunctionally.

2. The polyamides as in Claim 1, characterized in that they can be obtained by maintaining a molar ratio of component a) to component b) of at least 1 if component a) is trifunctional and component b) is bifunctional, and a molar ratio of at least 2, if component a) and component b) are trifunctional.

3. The polyamides as in Claim 1, characterized in that they can be obtained in that component a) contains bifunctional compounds in such a molar fraction that no more than 50 wt% of linear polymer chains form.

4. The polyamides as in Claim 1, characterized in that they can be obtained by simultaneously adding monofunctional compounds c) with a functionality corresponding to components a) in a molar fraction that does not exceed a).

5. The polyamides as in Claim 1, characterized in that they can be obtained by using monofunctional compounds c), which have the same functionalities as b), in a maximum molar fraction that is calculated based on the following formula

c) = $m_{a)}f_{a)} - m_{b)}f_{b)} + 100$.

wherein $m_{a)}$ and $m_{b)}$ stand for the molar fractions of compounds a) and b) (expressed in μmol/g polymer) and $f_{a)}$ and $f_{b)}$ stand for the functionalities of the compounds.

6. The polyamides as in Claim 1 as well as Claims 4 and 5, characterized in that they can be obtained by using monomer compounds according to a) and b) and by maintaining the conditions according to Claims 4 and 5 for the monofunctional compounds c).

7. The polyamides as in Claim 1, characterized in that they can be obtained by using trimesic acid or trimerized fatty acids as the at least trifunctional branching-causing carboxylic acid.

8. The polyamides as in Claim 7, characterized in that they can be obtained by using the carboxylic acid in the form of its esters.

9. The polyamides as in Claim 8, characterized in that they can be maintained by using a carboxylic acid ester of the formula listed below

19
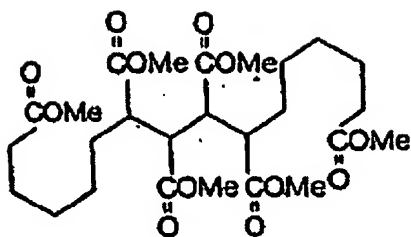
where Me stands for the CH$_3$ group.

10. The polyamides as in Claim 1, characterized in that they can be obtained by using (H$_2$N-CH$_2$-CH$_2$)$_3$N as the at least /17 trifunctional branching-causing amine.

11. The polyamides as in Claim 1, characterized in that they can be obtained by using
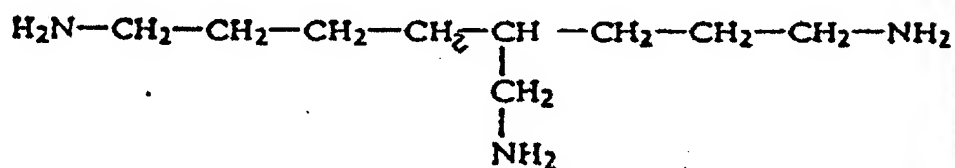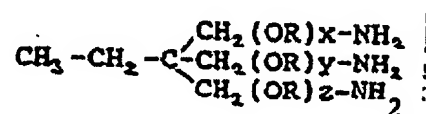
H$_2$N-(CH$_2$)$_x$NH (-CH$_2$)$_x$-NH$_2$ or

H$_2$N-(CH$_2$)$_x$NH (-CH$_2$)$_x$-NH -(CH$_2$)$_x$-NH$_2$ or

H$_2$N-(CH$_2$)$_x$NH (-CH$_2$)$_x$-NH -(CH$_2$)$_x$-NH -(CH$_2$)$_x$-NH$_2$,

where x stands for 2 to 13,

as the at least trifunctional branching-causing amines.

12. The polyamides as in Claim 1, characterized in that they can be obtained by using

as the at least trifunctional branching-causing amine.

13. The polyamides as in Claim 1, characterized in that

where x, y and z each stand for 1 to 15 and R is an ethyl, butyl or isopropyl group, as the at least trifunctional branching-causing amine.
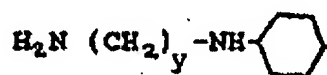
14. The polyamides as in Claim 1, characterized in that they can be obtained by using dicarboxylic acids, in particular adipic acid, dodecanoic diacid, isophthalic acid or terephthalic acid, as the at least bifunctional carboxylic acid b), and

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diaminobutane, diaminohexane, diaminododecane or a cyclic diamine, in particular 1,4-diaminocyclohexane, 4,4'-diaminobicyclohexylmethane or a 1,3- or 1,-4-xylylenediamine as the at least bifunctional amine.

15. The polyamides as in Claim 1, characterized in that they can be obtained by using chain regulators commonly used to regulate the chain length of polyamides, in particular benzoic acid, lauric acid, cyclohexylamine and isotridecylamine, as the monofunctionally active monomer c).
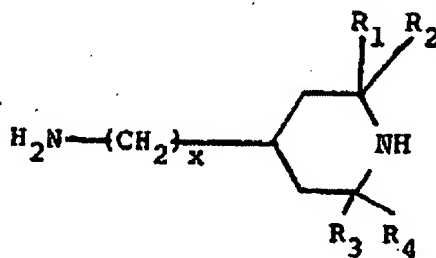
16. The polyamides as in Claim 1, characterized in that they can be obtained by using diamines with a condensable and a sterically hindered amino group as the monofunctionally acting monomers c).

17. The polyamides as in Claim 16, characterized in that they can be obtained by using diamines of the following formula

$$H_2N \ (CH_2)_y -NH-\hexagon$$

where y stands for 2 to 12, but is especially 3.

18. The polyamides as in Claim 16, characterized in that they can be obtained by using a diamine of the following formula

where x denotes an integral number from 0 to 12 and R_1, R_2, R_3 and R_4 are identical or different alkyl groups with 1 to 4 carbon atoms, in particular methyl groups.

19. The polyamides as in Claim 1, characterized in that they can be obtained by using caprolactam, enantholactam, laurolactam and/or the relevant aminocarboxylic acids and ω-aminoundecanoic acid and 4-(aminomethyl)benzoic acid alone or in combination with one another as the polyamide parent materials.

20. The use of the polyamides as in Claims 1 to 19, optionally in combination with conventional additives and auxiliary agents as molding compounds.
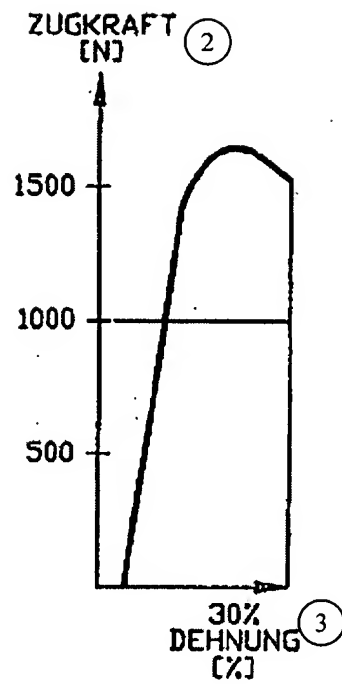
21

FIG.1

① Versuch 9

ZUGKRAFT ② [N]

1500

1000

500

235% DEHNUNG [%]

③
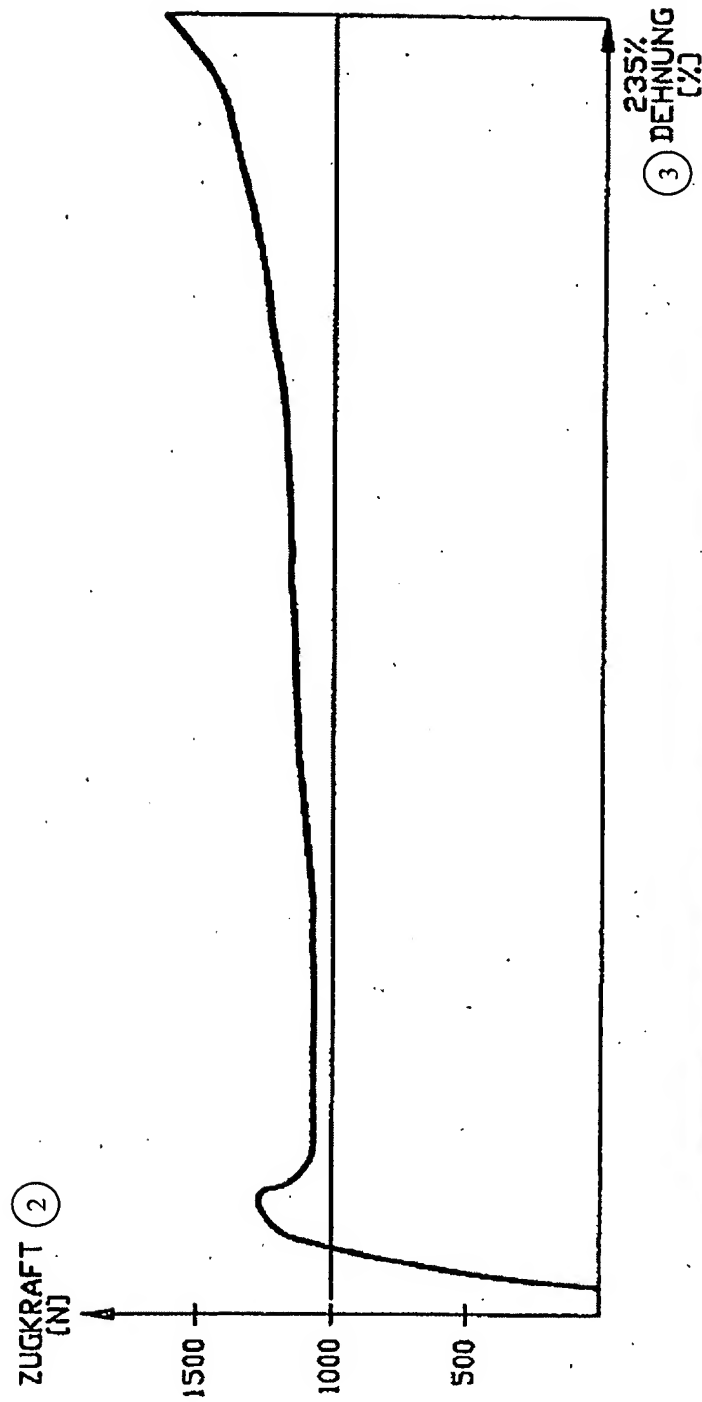
Key: 1 Experiment 9

2 Tensile strength (N)

3 235% elongation (%)

22

Figure 2

ZUGKRAFT ②
[N]

1500

1000

500

30% ③
DEHNUNG
[%]

Key: 1   Experiment 10

2   Tensile strength (N)

3   30% elongation (%)

Figure 3

① Versuch 12

② ZUGKRAFT [N]

1500 —

1000 —

500 —

32%
③ DEHNUNG [%]
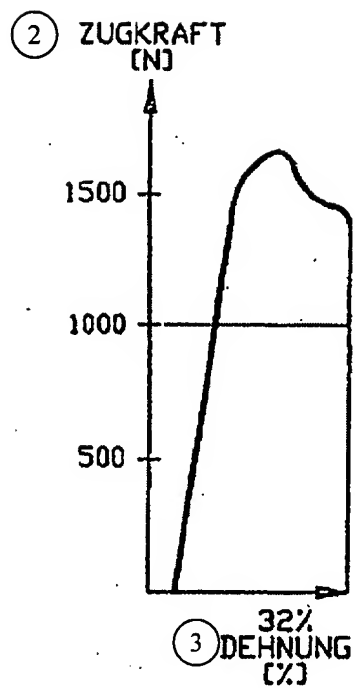
Key: 1   Experiment 12

2   Tensile strength (N)

3   32% elongation (%)

24
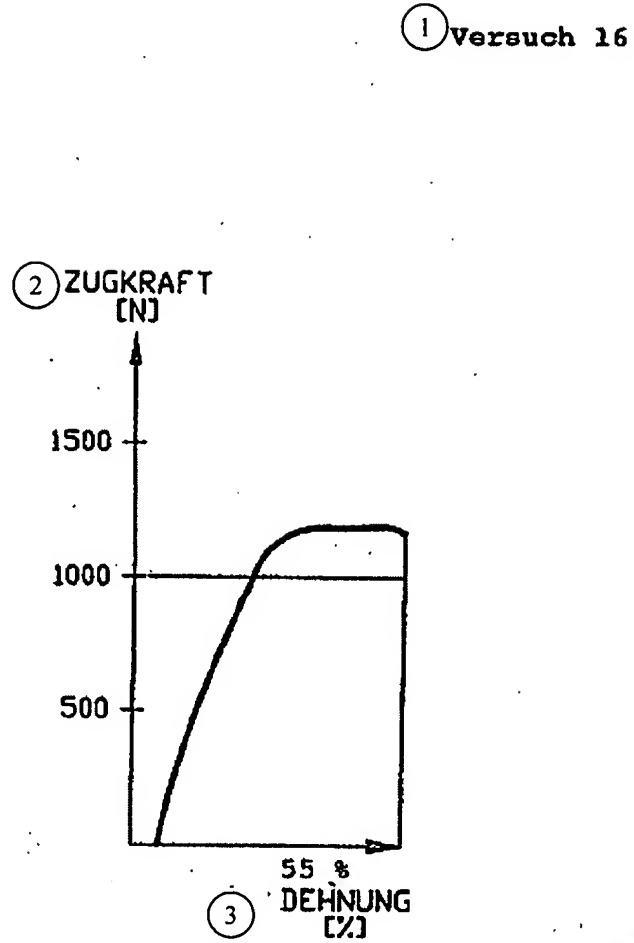
Figure 4

Key: 1   Experiment 16

       2   Tensile strength (N)
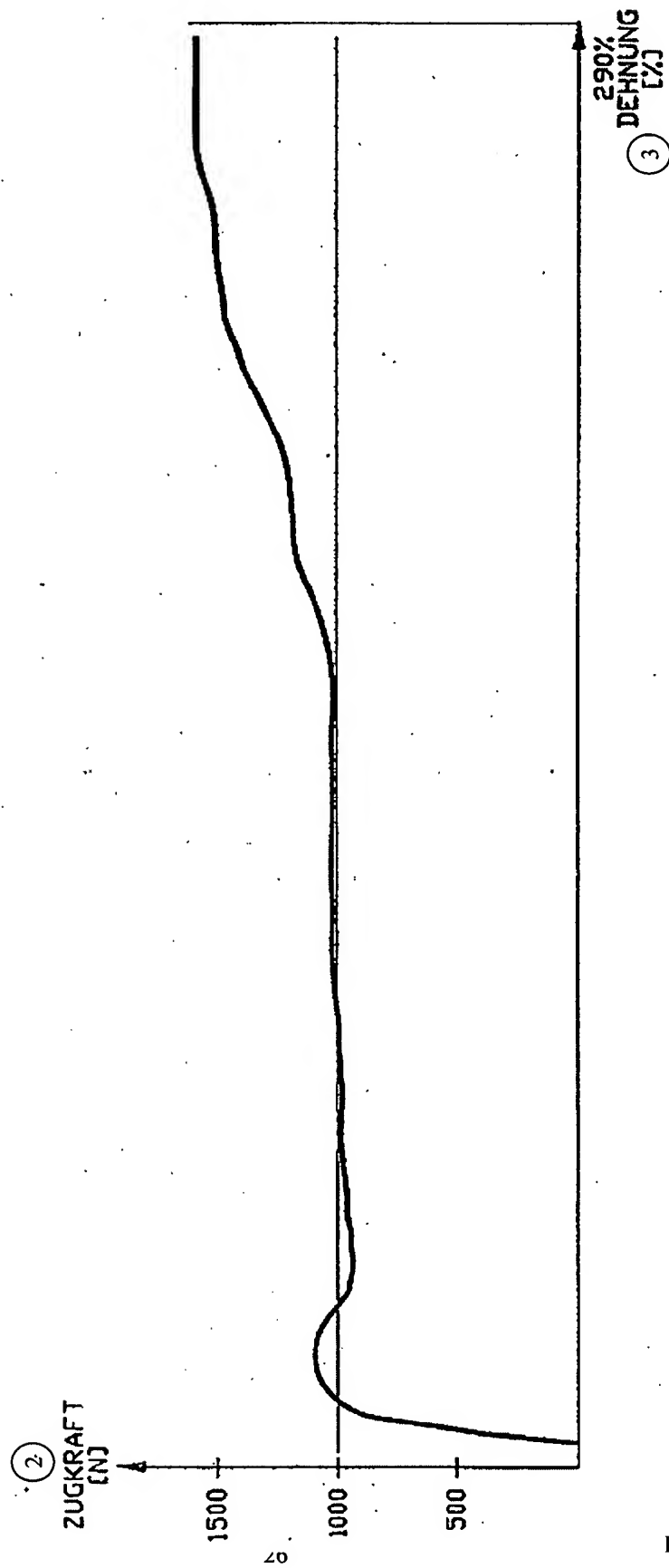
       3   55% elongation (%)

① Vergleichsbeispiel 19 PA 12

② ZUGKRAFT [N]

1500
1000
500

③ 290% DEHNUNG [%]

27

Figure 5

Key: 1 Comparative Example 19, PA-12

2 Tensile strength (N)

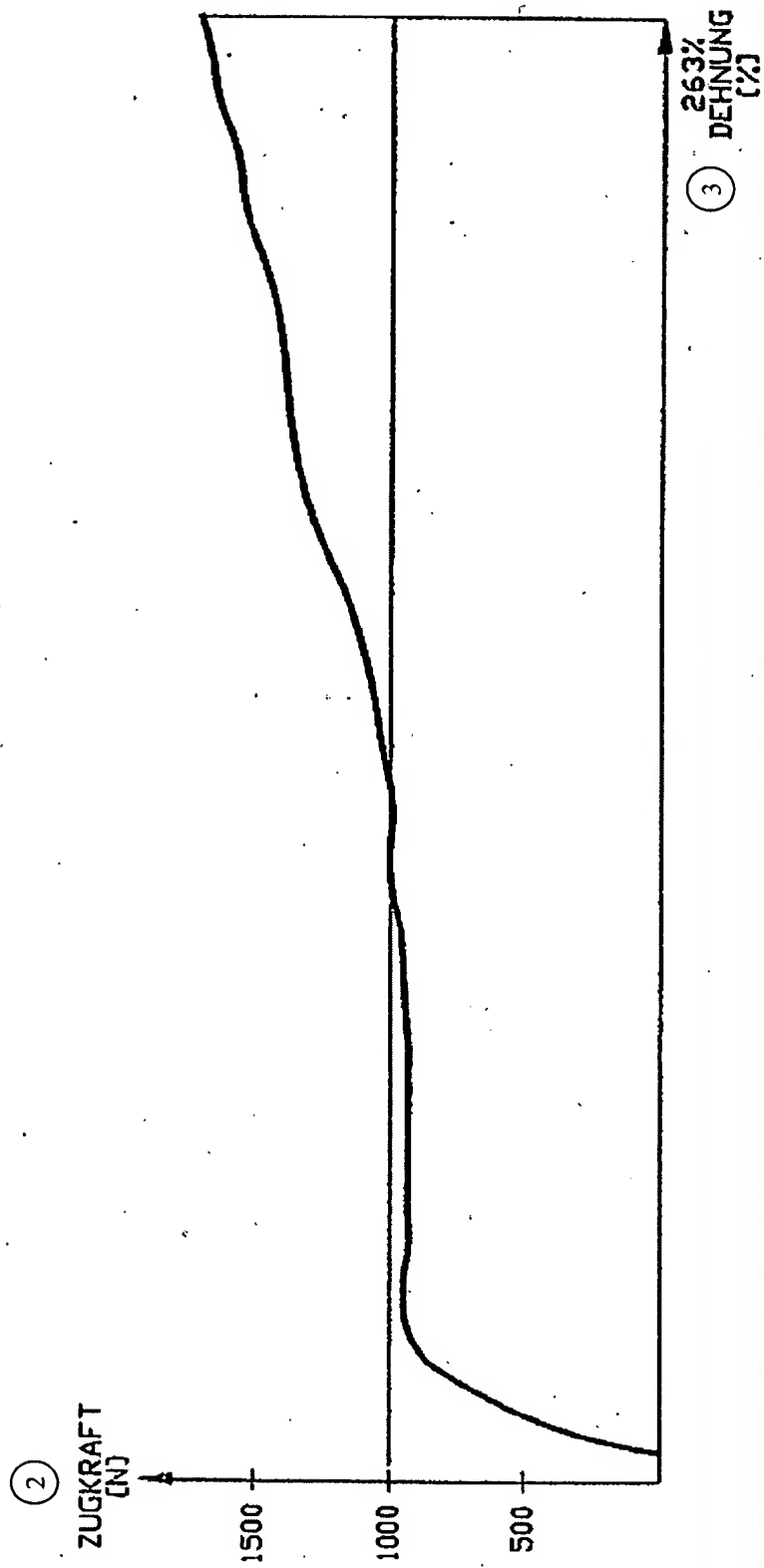3 290% elongation (%)

Figure 6

Key: 1 Comparative Example 20, PA-6

      2 Tensile strength (N)

      3 263% elongation (%)